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14. ABSTRACT

Porous silicon (PSi) has a high chemical energy, which has the potential to be converted to mechanical energy very quickly through ignition. Here we investigate a means to convert this mechanical energy to electrical energy via a piezoelectric cantilever and rectifying circuit. This current could be used to power sensors, devices, or store charge, and this type of system could be useful in ignition systems for munitions. The efficiency of this system is critical to realizing the potential for PSi as a one-time electrical energy source. A mechanical to electrical efficiency of 4.1% was achieved, but the chemical to electrical efficiency was much less than 1%.

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graphene oxide, GO, graphene, thermal reduction, supercapacitors, porous silicon, energy harvesting, piezoelectric cantilever

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1. Introduction and Background

Porous silicon (PSi) is a useful material for energetic applications because of its high surface area and reactivity. When silicon is etched, it creates pore networks that, when doped with an oxidizer and exposed to a source of ignition, rapidly combust.[1]

PSi has a high chemical energy, which has the potential to be converted to mechanical energy very quickly through ignition. Here we investigate a means to convert this mechanical energy to electrical energy via a piezoelectric cantilever and an associated rectifying circuit. A small PSi sample is placed on the cantilever, and when it is ignited, it bends the piezoelectric element, creating a usable current. This current could be used to power sensors, devices, or store charge, and this type of system could be useful in ignition systems for munitions. The efficiency of this system is critical to realizing the potential for PSi as a one-time electrical energy source.

2. Experiment and Calculations

2.1 Porous Silicon Preparation

P-type doped silicon wafers backed with platinum are patterned into 2-mm devices with bridge wires (Fig. 1 [left]). Using a silicon nitride layer as a mask, the silicon is etched using a galvanic etch process with hydrofluoric acid to make the PSi.[2] The depth and porosity of the PSi, which control the burn rate and intensity, were measured to be 22 µm and 71%, respectively (Fig. 1 [right]). PSi depth can be measured through scanning electron microscopy cross-section analysis or optical profilometry, and porosity is measured through nitrogen adsorption measurements with Brunauer-Emmett-Teller analysis.

The oxidizer being used is 3.2M sodium perchlorate in methanol (MeOH). Once the device has been placed in the experimental setup, 6 µL of oxidizer is applied to the pixel using a micropipette. It is important that the solution only be prepared and applied in a dry environment, as the perchlorate will absorb water and not dry or properly oxidize the PSi. The sample is left for 30 min for the MeOH to evaporate before the sample is ignited.

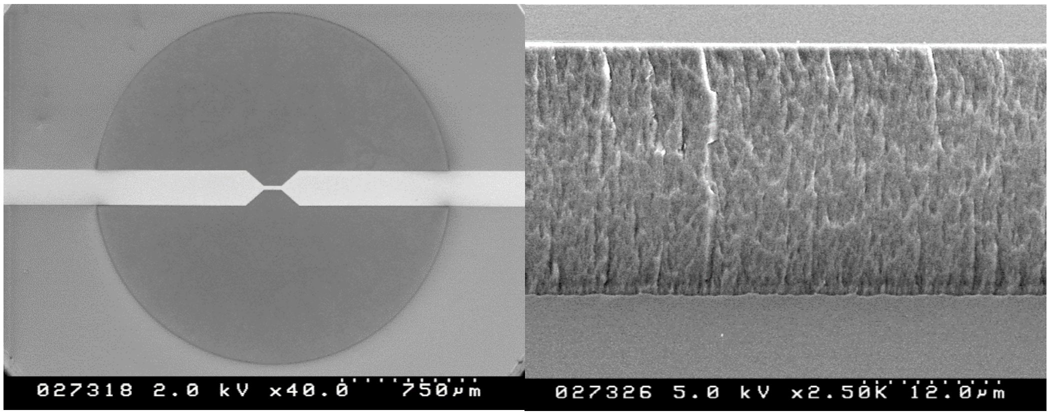

Fig. 1 Left: devices used were 2-mm pixel with bridge wires. Right: PSi depth measured to be 22 µm.

2.2 Experimental Setup

The setup for this experiment is illustrated by Fig. 2. The 2-mm pixel PSi sample is attached to a small device package using carbon tape and is wire-bonded to the pads on the package. Thin wire leads connect the holder to the ignition power source. The holder is then placed on the end of the piezo cantilever.

The piezo cantilever being used is a Volture V22B, purchased from Midé. This 4-pin, 2-element piezo cantilever is wired to a direct current (DC) full-bridge rectifier circuit (EHE001NC) also purchased from Midé. Test points have been added at the output of the cantilever so that measurements of the alternating current (AC) signal can be taken easily.

The DC output from the rectifier can be used to power a device or sensor. In this case, as a proof of concept, we are using it to charge a capacitor to store the energy for future use. The voltage across this capacitor is measured using a Tektronix DPO2014 oscilloscope with standard 1x probes. Alternatively, we measure the voltage by connecting a digital voltmeter (DVM) to the capacitor after all of the energy has been stored. This allows us to measure the stored energy without losses due to the oscilloscope input impedance.

The size of the capacitor used is very important because the capacitor size affects how much energy is stored. If the capacitor is too small, then it will quickly charge to a voltage above the cantilever output so no further energy storage is possible. If the capacitor is too large, the stored energy will be lower because the piezoelectric current will charge the capacitor to a lower voltage, with energy in a capacitor being proportional to voltage squared:

$$E = \tfrac{1}{2} CV^2 . \qquad (1)$$

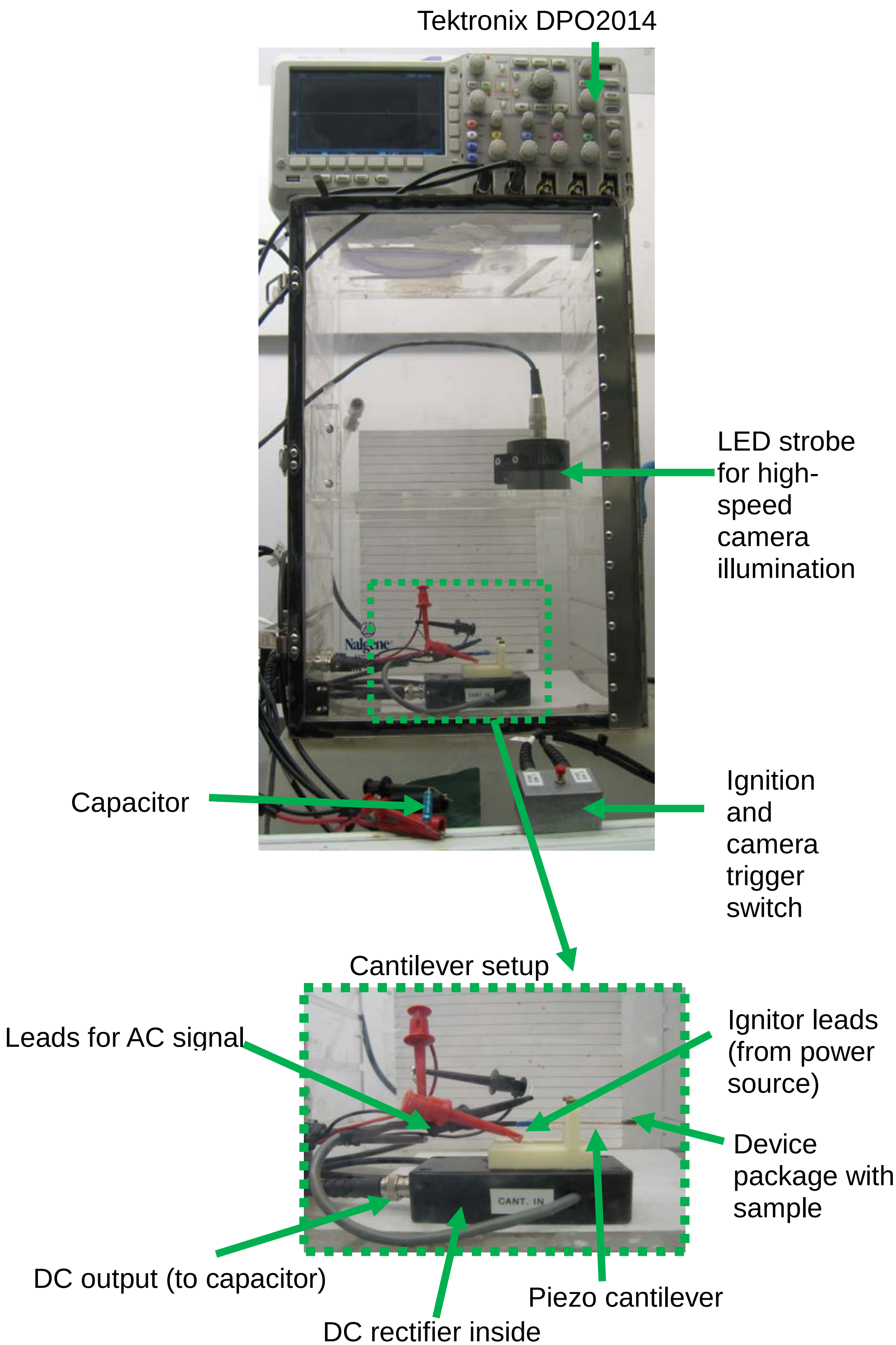

Fig. 2 **Experimental setup for testing PSi samples on a piezo cantilever and analyzing the electrical output**

To select the most efficient capacitor, known weights were dropped onto the cantilever (simulating the force from one of our devices) while it was hooked up to the capacitor. The resulting voltages were measured using the oscilloscope, and energies were calculated using Eq. 1. Capacitors between 0.01 µF and 60 µF were tested with this method. Initially, a 0.25-µF capacitor was chosen because of its superior peak energy capture; however, the higher voltage results in more energy lost due to reverse current across the rectifier diodes. Thus, we moved to using a 2.5-µF capacitor for energy storage. It is important to balance the voltage on the capacitor with the current losses in the system to maximize efficiency.

2.3 Energy Calculations

The goal of this setup is to convert as much mechanical energy from the PSi as possible to electrical energy. To get a rough idea of how much mechanical energy is produced by the PSi, we can use the equation for strain energy in a cantilevered beam:

$$U = \frac{1}{2EI} \int M^2 dx \ . \qquad (2)$$

Here, the mechanical energy in the cantilever (*U*, joules) is related to the flexural stiffness *EI*, where *E* is the Young's modulus, and *I* is the second moment of inertia. These values were determined using product data from the manufacturer of the cantilever, where $E = 6.7E10\ N/m^2$ and $I = 1.53E\text{-}13\ m^4$. Energy is also proportional to the integral of the force moment on the end of the cantilever, *M*, which is equal to the force multiplied by the distance between the applied force to the fixed point of the beam. For example, based on data from Churaman et al.,[3] we expect that these 2-mm devices with 22-µm PSi depth should output 600 mN of force. The strain energy in the cantilever under this force, assuming the moment is acting at 2.5 cm from the fixed point of the cantilever, will thus equal (according to Eq. 2) 117 µJ.

To determine the electrical energy captured, we calculated the energy stored in the capacitor (using the voltage measured with the oscilloscope or DVM, though the latter tended to provide more accurate results) using Eq. 1, and then compared it to the strain energy. This provided an estimate of system efficiency from ignition to charge storage.

3. Results and Discussion

Electrical energy conversion relies heavily on the mechanical force output of the PSi devices. While some samples did indeed provide the approximately 600-mN force as Churaman et al.[3] saw with their samples, other samples provided much lower outputs. Testing of our samples on a load cell showed that device outputs varied from 100 mN to 600 mN. The source of this variation is the subject of ongoing investigations.

For high-output devices (~600 mN), the capacitor was usually charged to approximately 1 V, which corresponded to an energy storage of 1.25 µJ and a mechanical force to stored electrical energy efficiency of 1.1%.

On the low end of device output (~100 mN), the voltage across the capacitor was measured to be approximately 0.3 V, corresponding to an electrical energy storage of 0.11 µJ and an efficiency of 4.1%. Because the energy stored on the capacitor was proportional to V^2, energy storage was affected by an order of magnitude for these devices. Despite the lower force number here, and the lower electrical energy storage, the efficiency number was actually higher because of the square factor of the moment in Eq. 2. The efficiency number remained roughly the same (within a similar order of magnitude) because the decrease in ignition force is similar to the decrease in energy storage.

The AC signal output from the piezo, shown in Fig 3, is useful for looking at the behavior of the cantilever during ignition. If higher-order harmonics in the cantilever are excited by the force of the PSi reaction, extra modes will be excited in the fixed-beam system, which will decrease overall efficiency because of opposing currents being generated within the piezo.

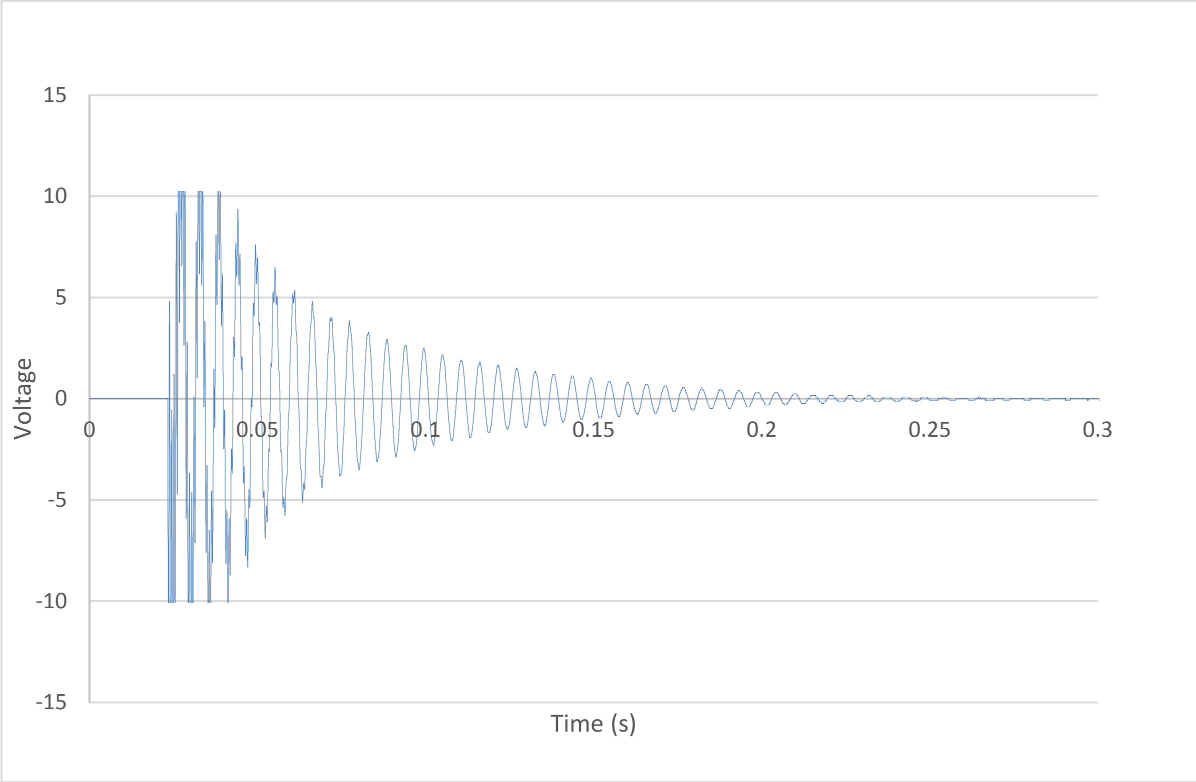

Fig. 3 Damped oscillation AC signal from the cantilever

To investigate this, we looked at how sample placement affected the performance of the system. If the sample was placed too far forward or too far back on the piezo cantilever, higher-order harmonic modes were excited in the beam, which led to destructive interference in the AC output (e.g., Fig. 4) and overall lower energy output. Optimal placement of the sample is located at a distance 76% of the total length of the beam, as determined by Euler-Bernoulli beam theory (Fig. 5), which will take advantage of the first and second harmonic modes of the cantilever. Samples were tested at this location, as well as in front and in back of this position. It was found that, as expected, if the sample was placed too far forward, multiple modes were excited in the beam, and a lower overall signal occurred due to destructive interference. The multiple excited modes are also visible in high-speed camera footage of ignitions. For samples placed behind the optimal location, a smaller deflection occurs, leading again to a smaller energy output from the cantilever.

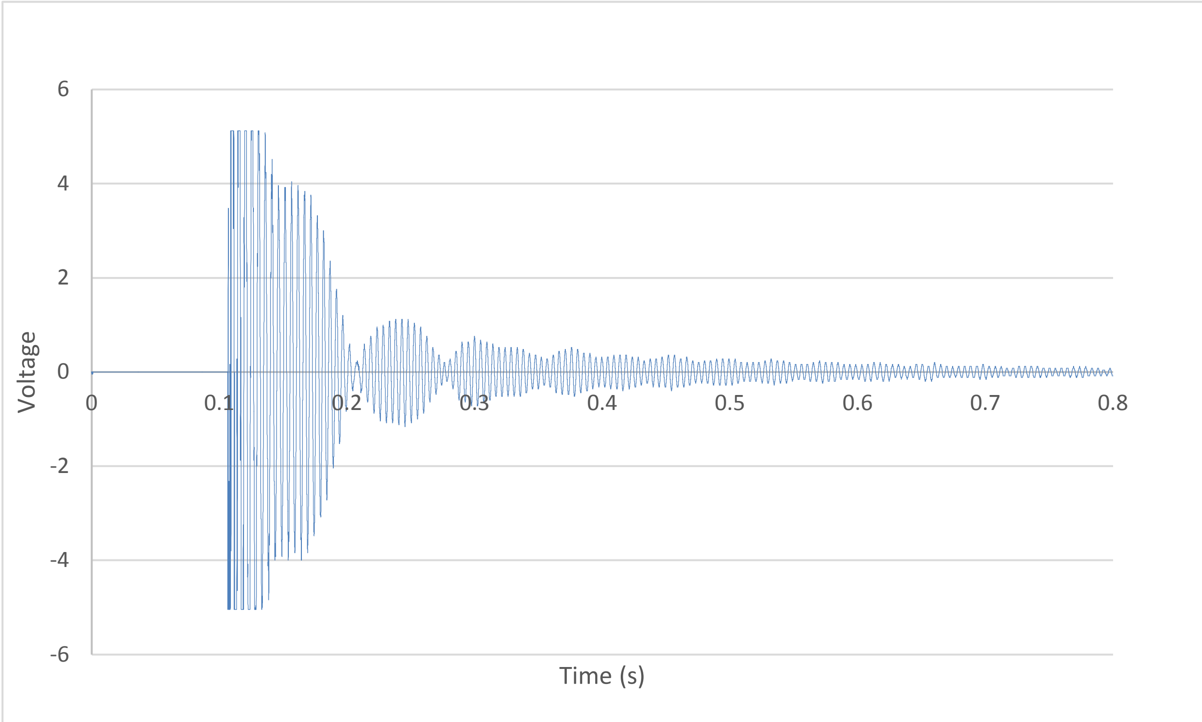

Fig. 4 **Example of destructive interference in the AC signal output**

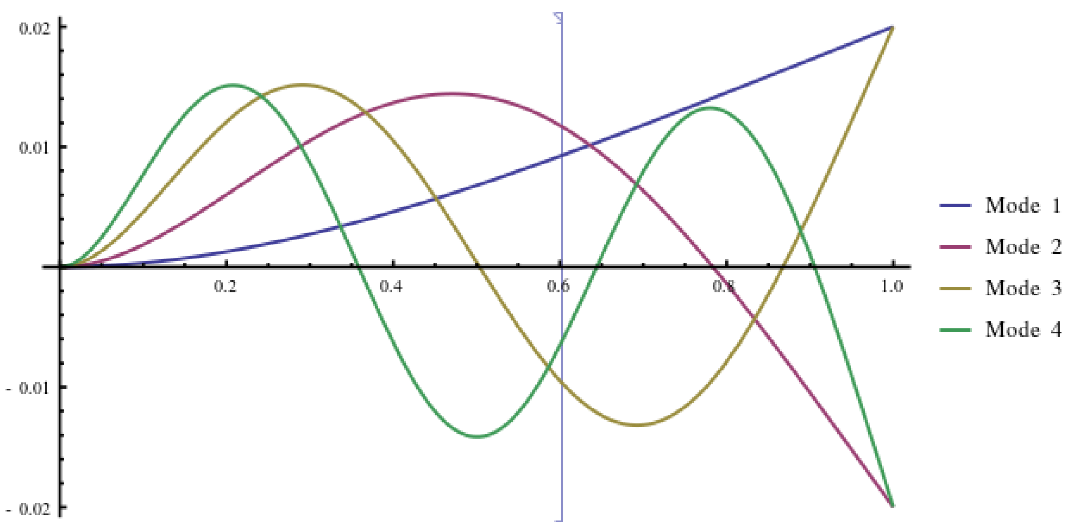

Fig. 5 **Displacement of a cantilevered beam. Sample placement at the node of the harmonic curve is optimal for energy harvesting. Sample placement at the node for mode 2 provided the best results compared to sample placement at the end of the cantilever. (Image from Wikipedia: https://en.wikipedia.org/wiki/Euler%E2%80%93Bernoulli_beam_theory)**

4. Conclusions

We have demonstrated a proof-of-concept system that harvests electrical energy from PSi combustion. The efficiency from the mechanical energy of the PSi to the electrical energy storage in a capacitor ranges between 1.1% and 4.1%, depending on the yield of the PSi devices. This efficiency could be improved in a number of ways, including changes to the system as well as the devices. Overall, this translates to a chemical energy to final electrical energy efficiency of less than 0.0001%, assuming the chemical energy of PSi to be 9.2 kJ/g.[1] This poor chemical- to electrical-energy efficiency conversion makes it apparent that it will be very difficult to efficiently use the high-energy density of PSi to efficiently produce electrical energy.

The most significant issue with this experiment is that the device mechanical force output was not consistent. Unfortunately, with such a wide range for device force output, it is difficult to select the appropriate-sized capacitor to store charge from ignitions. This made it difficult to get an idea of the realizable efficiency of our system. The cause for inconsistent yields is currently under investigation.

It was also found that sample placement on the cantilever affected the energy stored on the capacitor. The mechanics of the cantilever are optimized when the device is placed at a harmonic node of the cantilever, so that no destructive interference is produced and the cantilever has maximum deflection. Destructive interference in the cantilever AC signal was shown to have negative effects on the energy output, but this can be fixed with proper sample placement.

There are a few ways that the system could be further improved to increase efficiency:

- Tuning the piezo cantilever to excite only the fundamental mode leading to more overall energy output.
- Optimize the mechanical coupling of the sample output to the cantilever, and reducing losses due to nonactive materials in the cantilever (the Kapton coating).
- Directing the force of the device through a nozzle to create more thrust perpendicular to the cantilever and reduce the amount of torsion in the cantilever beam, which may induce destructive interference.

While the energy conversion efficiencies are low, this setup could prove to be a useful tool for device characterization. Through the analysis of the AC output of the piezo cantilever, one could determine the mechanical force output of a PSi device.

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